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Radical polymerisation process and additives for synthetic resins so prepared.

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Abstract of EP0035729 (A2)

A process for the free-radical polymerisation of acrylic acid and methacrylic acid, esters and amides thereof, acrylonitrile and styrene using a liquid medium which is a melt of organic compounds which are solid at room temperature, preferably saturated or unsaturated, straight-chain or branched fatty acids having up to 30 (from 8 to 26) carbon atoms, or derivatives thereof (esters, amides or fatty alcohols) having drip points of between 25 and 120 DEG C (40 to 110 DEG C). The ratio by weight between the monomers and the solid organic compounds is from 10 to 90:90 to 10 (25 to 75:75 to 25). The process allows the direct preparation of plastics additives for plastics processing, specifically for the processing of elastomeric, thermoplastic polymers and thermosets, in particular by thermoforming.

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Description EP0035729

[0001] The present invention relates to a process for free radical polymerization of unsaturated monomers using inert diluents, such as reaction medium. The new process allows the production of polymer-containing compositions which can be further processed for many purposes without removal of the polymerization. In particular, the invention relates to a process for free radical polymerization of acrylic and methacrylic acids, their derivatives and Styrol. The knowledge gained by the novel method polymer-containing compounds are highly effective additive systems for the plastics processing, especially for the processing of polyvinyl chloride dar

[0002] In the bulk polymerization of the monomers are polymerized without dilution medium and go through the viscous liquid from the solid state. The need for all polymerizations heat of reaction is here, especially for very reactive monomers such as methyl acrylate, acrylic acid or ethylene tetrafluoroethylene a difficult problem to solve dar. Moreover, the obtained polymer can be removed only with difficulty because of their high viscosity of the reaction vessel and processed.

[0003] In solution, the monomers, dissolved in the solvents used, the resulting polymers can be soluble or insoluble. The solvents used in the practice of water or low molecular weight organic solvents such as aliphatic or aromatic hydrocarbons, esters, ethers, alcohols and ketones. The viscosity of the reaction mass in the solution is much lower than in the case of bulk polymerization, however, requires a considerable amount of additional costs not only for facilities for the removal of the solvent from the polymer, but also for the recovery and purification of the solvents. Polymers are usually produced by this method only if the solutions are used as such, for example, paints and adhesives, the polymers in the liquid thus means that in the dissolved state gets used.

[0004] The present invention was to find liquid polymerization media, which are liquid at normal polymerization temperatures, but are at room temperature or at the temperature of processing powdery or waxy solids, and so further processing of the polymer as a solid mass, while avoiding a separation operation permit from the usual liquid polymerization medium. Another specific object of the present invention was to find such a polymerization media, the finding for the synthesis of polymeric additives for the plastics processing as a flow promoters or release agent or other plastic additives on acrylic and methacrylic esters and styrene-based, with the solid at room temperature polymerization an inert material with no negative effects or even a second active component for the further process of the plastics processing represents.

[0005] According to the invention this object is achieved by a process of free-radical polymerization of unsaturated monomers using inert diluent, which is characterized in that the polymerization is carried out in the melt of solid organic compounds at room temperature. Preferably, the polymerization at room temperature, solid fatty acids or their derivatives with dropping points 25-125 [deg.] C., particularly between 40 and 110 [deg.] C performed (see "fats, soaps, paints" (1954), p. 1028). Those responsible for the polymerization of suitable fatty acids are solid at room temperature, in particular up to 30 carbon atoms in the molecule. This is also true for their derivatives such as esters, amides and / or fatty alcohols.

[0006] A particularly preferred group are saturated or unsaturated, linear or branched fatty acids with 8 to 26 carbon atoms in the molecule and / or derived therefrom ester and / or partial esters of mono- to hexafunctional aliphatic or cycloaliphatic alcohols and / or fatty acid amides, where the nitrogen may be substituted with 1 to 2 alkyl groups with up to 16 total carbon atoms. Optionally, the alkyl radicals are also part of the nitrogen as a ring.

[0007] The fatty acids are suitable for the process - as stated before - up to 30 carbon atoms, but preferably contain 8 to 26 carbon atoms in the molecule. They can also double bonds can be contained and linear and branched. It is also possible that these fatty acids are substituted with one or two hydroxyl groups or some chlorine atoms.

However, the number of chlorine atoms does not exceed the number 6. Suitable fatty acids can be produced from natural materials or synthesized in known way. Also suitable are the so-called Montan acids, which have slightly longer chains up to 30 carbon atoms. In addition to the fatty acids themselves suitable are the esters or partial esters of mono-aliphatic or cycloaliphatic alcohols to hexafunctional. Suitable alcohols with the mono-alcohols up to 18 carbon atoms, especially methanol, ethanol, propanol and butanol. Among the polyhydric alcohols are: the ethanediol, glycerol, trimethylopropane, pentaerythritol, sorbitol or mannitol. Unless there are derivatives of fatty acids with polyhydric alcohols, the hydroxyl groups can be only partially esterified. Suitable cycloaliphatic alcohols, for example, the cyclohexanol or 1,4-cyclohexanediol.

[0008] The inventive method suitable for the amides derived from those projected, characterized from fatty acids. Here, the nitrogen with 1 to 2 alkyl groups may be substituted. Substituents on the nitrogen out of the question methyl, ethyl, propyl, butyl and octyl. If the radicals are joined to form a ring, the ring 5, and 6 is preferred.

[0009] According to another preferred embodiment, the inventive polymerization in aliphatic natural or synthetic, optionally double bond contained mono alcohols with 8 to 26, made preferably 8 to 18 carbon atoms in the molecule.

Also suitable are esters of mono- and dicarboxylic acids.

The above-mentioned mono-alcohols may have from 1 to 2 double bonds and are characterized by reduction of the corresponding fatty acid alkyl esters, particularly fatty acid methyl esters are readily available.

As esterifying come alongside short-chain mono carboxylic acids such as acetic acid or propionic acid in question dicarboxylic acids such as adipic acid, sebacic acid and terephthalic acid.

[0010] If the conditions are met in accordance with the dropping point, numerous derivatives of fatty acids and fatty acid itself suitable.

An overview of such compounds is found in the journal "Plastics, Plastics," 3 (1975), p. 17 ff and in the magazine "Plastics" 66 (1976), p. 697.

[0011] Suitable monomers for the method of the invention are suitable ethylenically unsaturated such types such as acrylic acid, methacrylic acid and their esters, acrylonitrile, (meth) acrylamide, or styrene. The following may be mentioned here: acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, acrylic acid-2-ethyl hexyl acetate, ethyl methacrylate, butyl methacrylate and the esters of butanediol, ethylene glycol or Tetrahydroxyalkohol with acrylic acid or methacrylic acid.

Furthermore, the ideal self and acrylonitrile, acrylamide, which may be substituted on the nitrogen, such as the Methylacrylamid or isopropylacrylamide or the tert-butyl acrylamide.

Other suitable monomers such as [alpha]-methyl styrene, p-chloro styrene or ethyl styrene, divinylbenzene, dicyclopentadiene and isoprene as well as

[0012] Preferred monomers or monomer mixtures, polymers or copolymers which are effective additives for the plastics processing, specifically for the thermoplastic processing of polyvinyl chloride.

It is for methyl methacrylate, methyl methacrylate and butyl acrylate, and mixtures of ethyl acrylate, methyl methacrylate also mixtures of acrylic acid, butyl methacrylate and styrene way relationship.

For example, for the production of a so-called flow promoters and ethyl acrylate, a copolymer of methyl methacrylate suitable.

A polymer of butyl acrylate is also suitable as release agents in the processing of polyvinyl chloride, when certain known proportions are maintained.

[0013] The inventive method used by the inert diluent of the polymerization temperatures have relatively low to medium viscosity maximum.

They are so easy to stir liquids.

Therefore, the removal of polymerization is relatively easy and even greater approaches can be well controlled.

The weight ratio of monomers to the solid at room temperature inert diluents should be between 10: 25 are 90 and 90: 10, particularly 25: 75 and 75.

Practically, it is determined by the desired properties of the polymer-containing composition containing the final product.

[0014] Suitable initiators for the polymerization are the known conventional radical initiators such as peroxides, for example, diacetyl peroxide, benzoyl peroxide or hydroperoxides such as cumene hydroperoxide.

However, azo compounds are preferred as azobiscybonitrile.

The polymerization is carried out so that the appropriate solid inert diluent are presented and melted.

This one is then at the desired reaction temperature, the monomer.

Usefully you can in the monomer or monomer polymerization initiator distributed run slowly.

We choose such an initial temperature, the polymerization starts rapidly.

In batch polymerization, the reaction generally after 2 to 6 hours is completed.

[0015] Of course it is also möglich to carry out the polymerization continuously, for example, the first part in a reaction tube, where it feeds the liquefied inert diluent simultaneously with the monomers to be polymerized.

Here, the initiator at once or at different locations may be added.

After performing the first reaction step, then a secondary reaction in a collecting vessel is possible.

[0016] In the case of acrylic and methacrylic acid esters of lower alcohols such as ethyl acrylate and methyl methacrylate or in the case of polymerization of styrene, the polymerizations run as a dispersion or precipitation polymerization.

The monomers are soluble in the melt of the fatty alcohol and fatty acid derivatives, the polymers are insoluble.

Depending on the reaction you get more or less finely divided polymer precipitation or finely divided suspensions with particle sizes between 0.1 [micron] up to 3 mm.

[0017] The copolymerization of such monomers, which form soluble and insoluble polymers, for example, in the copolymerization of methyl methacrylate and butyl methacrylate, go through the sticky phase polymerization, which can lead to unwanted clotting.

In these cases, the concomitant use of 0.1 to 15 weight percent, based on monomer, a special emulsifier proved advantageous, since it effectively prevents both the coagulation and the particle size influenced.

Such emulsifiers for non-aqueous systems, such as polymers or graft copolymers of methyl methacrylate with lauryl methacrylate or ethylhexyl acrylate or poly-2-ethylhexyl acrylate itself and its copolymers with other acrylic and methacrylic monomers.

An overview of suitable emulsifiers are, for example, Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York, "Non-aqueous dispersions."

[0018] prepared by the method of the invention are polymers in the molecular weight ranges from about 500 to 5 000 000, in particular, 1000-500000, wherein the polymerization is usually exerts a weak Telogenfunktion.

Ely further use of typical telogens such as aliphatic mercaptans can the molecular weights - such as from other known polymerization processes - reduce.

The concomitant use of di- and multi-functional monomers such as divinylbenzene, dicyclopentadiene or increase the molecular weights up to the formation of insoluble gels.

[0019] The resulting polymer-containing compositions are included, depending on the type of polymers and the fatty alcohol and fatty acid derivatives and, depending on the weight ratio of both components contained waxy solid to powdery products.

The workup of the melting or smelting is done advantageously cooled by spray cooling from the processing or other waxy fatty acid derivatives of known methods.

In many cases, you can grind the polymer-containing compounds at room temperature or under refrigeration if necessary to fine powders.

[0020] The results obtained in the inventive process, reaction products are valuable synthetic additives that can be used for processing of thermoplastic and thermosetting polymers are used under hot deformation.

In particular, the invention according to available plastic additives for thermoplastic processing of polyvinyl chloride or copolymers of vinyl chloride are suitable.

Apart from this main use they can of course also in the processing of thermoplastic polymers used by others if proper conditions are met.

These are given under certain circumstances in the processing of polypropylene, polyethylene, copolymers of ethylene with vinyl acetate, polymethacrylates, copolymers of methyl methacrylate with other monomers, polyurethanes, polyamides and particularly linear polyesters.

Examples

The polymers

[0021] In a 2-l-Planflanschapparatur glass with stirrer, thermometer and dropping funnel were placed at room temperature and solid fat derivatives by heating to 30 to 120 [deg.]

C. liquefies.

In the course of 2 to 6 hours dripped the monomers and the polymerization initiator to be evenly and allowed to react for 30 minutes to complete the conversion.

In some cases, is added to the molten polymeric emulsifiers or protective colloids to obtain finely divided polymer emulsions or suspensions to

The cooled polymer-containing composition was pulverized by grinding or shed

[0022] In the following table are given after the serial number of the example, the reaction medium, the monomer, the initiator (AIBN = azobisisobutyronitrile, DA: = diacetyl).

As an emulsifier was always poly-2-ethylhexyl acrylate is used, if one proved necessary.

This is followed by polymerization temperature and duration.

This gave a solid homogeneous solutions or fine dispersions.

[0023]

Application of the products

[0024] The products produced by the above examples were good lubricant or release agent.

The product of Example 6 and 8 was a so-called "flow-promoter" used, meaning that it conveyed an inner sliding in the processing of PVC and thus reduced the plasticizing

[0025] The product of Example 4 was examined in more detail on his release and lubricating properties. The experiments were performed on a laboratory rolling mill at a roll Benstoff dimensions of 450 x 220 mm.

a) The following approach has been made:

On the rolling mill were made furs and the time up to stick to the roll

When using the comparison mixture was tack-free time of 1 minute, with the inventive product used in Example 4 38 minutes.

Then the experiment had to be canceled because the thermal stability of the strip was finished.

The experiments were [deg.] At a roll temperature of 200

C made

b) A basic approach has been established:

The experiment was [deg.] At a roll temperature of 195

C made.

The comparison as a lubricant mixture contained 1 part by weight of glycerol mono oleate, 5.5 parts by weight of fatty acid esters of octylphenol, 1 part by weight of a copolymer of methyl methacrylate and ethyl acrylate.

Was used for comparison in a second trial, the product of Example 4 in the same amount.

It was the pressure in the nip measured at different speeds and get the following results:

c) The product of Example 7 was carried out following comparison test.

[0026] In one Plasticorder Brabender was the mixture at 165 <(t> C and examined at 30 rpm.

It has been compared as a lubricant used 2 parts by weight of phthalic acid di-ester of a C16/18-

Fettsäuren and 1 part by weight of a commercially available copolymer of methyl methacrylate and ethyl acrylate

[0027] In contrast, three were then threaded axle parts used in Example 7 of the manufactured product.

It was shown that the used sample with this product as desired non-plasticized, because the sliding action was very high.

Under the same conditions, the comparison sample was plasticized after 2.7 minutes



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Claims EP0035729

First

Process for free radical polymerization of unsaturated monomers using inert diluent, wherein the polymerization is carried out in the melt of solid organic compounds at room temperature.

Second

The method of claim 1, wherein the polymerization at room temperature, solid fatty acids or their derivatives with dropping points 25-120 [deg.]

C., particularly between 40 and 110 [deg.]

C is performed.

Third

Method according to claims 1 or 2, wherein the polymerization is carried out in the melt of fatty acids are solid at room temperature for up to 30 carbon atoms and / or their derivatives such as esters, amides and / or fatty alcohols

4th

Method according to claims 1 to 3, characterized in that the polymerization in the saturated or unsaturated, linear or branched fatty acids with 8 to 26 carbon atoms in the molecule and / or derived therefrom esters and / or partial esters of mono-to hexafunctional aliphatic or cyclicaliphatic alcohols and / or fatty acid amides, the nitrogen, with 1 to 2 alkyl groups with up to a total of 16 C can be substituted carbon atoms, is made.